Effect of humidity and flue gas impurities on CO2 permeation of a polymer of intrinsic microporosity for post-combustion capture

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Abstract

The impact of humidity and flue gas impurities on PIM-1 membrane performance for post combustion capture, i.e. CO_2 permeability and CO_2/N_2 selectivity, is investigated in this study. The presence of humidity in the feed stream induces a decrease in the permeability coefficients of both CO_2 and N_2, from 7010 Barrer (dry state) to 4135 Barrer (%RH=50%) and 360 Barrer (dry state) to 250 Barrer (%RH=50%) respectively. PIM-1 shows also a high water permeability (58800 Barrer) which increases with the relative humidity of the feed. The interaction with flue gas contaminants (NOx, SOx, Water) leads to a dramatic decrease of the membrane performance even after short exposure and FTIR analysis confirmed modifications of the chemical structure of PIM-1 caused by the acid environment. These results indicate that test with flue gases have to be considered for all novel materials proposed for carbon capture applications since the decrease in membrane permeability in presence of water and other impurities has to be taken into account during the design of the separation process.

Highlights

- Effects of water and flue gas on PIM-1 performance are investigated.
- The addition of moisture in the feed induces a decrease in the CO_2 and N_2 permeability.
- The interaction with NOx and SOx leads to a decrease of the membrane performance.
- The observed decline in permeability has to be considered in designing the separation process.

Keywords

PIM-1 membrane, CO_2 capture, gas permeability, water permeability, flue gas.

1. Introduction

The capture of carbon dioxide from large emission point sources is considered as a key mean for the mitigation of greenhouse gases emissions (Davison, 2007). Consequently, carbon capture and storage (CCS) is actively investigated through different strategies and processes. More specifically, the CCS technological chain involves three major steps: separation of CO_2 from a gaseous stream; compression and transport; and geological storage in an appropriate location. A large number of studies (Allam, 2003; Krishnamurthy et al., 2014; Yazdanfara et al., 2015; Leimbrink et al., 2015; Spigarelli and Kawatra, 2013) are dedicated to the design of the most efficient carbon dioxide separation process that still represents 60 to 80% of the cost of the overall CCS chain. For post combustion CO_2 capture, several technologies have been proposed including absorption, adsorption, cryogenic distillation, and membrane separation (Allam, 2003). Packed columns with amine solutions represent the most mature technology but they are very energy intensive and suffer from various problems including flooding, foaming and/or solvent degradation. Membrane separations present many advantages, like compactness, and easy integration in already operating facilities (Ho et al., 2008; Abanades et al., 2015). As the post-combustion flue gas is released at low pressure (lower than 1.5 bar), highly selective and highly permeable membranes are required (Han and Lee, 2011) to have high efficiency in the separation process.

Polymers of intrinsic microporosity (PIMs) have attracted a lot of attention for this application in recent years (Budd et al., 2008). The very rigid and contorted backbone of PIMs induces unusually high free volumes and high internal surface area. PIM-1, the first reported high molecular weight microporous ladder polymer, has demonstrated extremely high gas permeabilities with moderate ideal selectivity (Budd et al., 2005; Li et al., 2012; Thomas et al., 2009; Li et al., 2013; Bushell et al., 2013), especially for O_2/N_2, CO_2/N_2 pairs with values lying above the Robeson's upper bound (Robeson, 2008). Therefore PIM-1 shows promise for membrane separation modules, especially for CO_2 removal.

Most of these results were obtained under ideal conditions with pure gases and do not represent the separation performance in real plant conditions. Indeed, membranes for gas separation have to be tested in mixture conditions especially for highly plasticizing gases like CO_2. Moreover flue gas contains other components and impurities, which differ according to the origin of the flue gas and can impact the transport properties of the membrane. For example, the flue gas from a coal fired power plant contains significant amount of water (11 mol%), oxygen (4 mol%) and also NOx and SOx at ppm level. As pointed out in a recent review on emerging CO2 capture systems (Abanades et al., 2015), impurities must be taken in account in order to carry out an accurate analysis of the real separation potential and design carbon capture processes based on membrane technology that are deployable at commercial scale.

Water vapour is expected to have very strong impact on the membrane transport properties, because of its very small size and its high hydrogen bonding affinity. For rubbery polymers, the gas permeability increases strongly with the permeate water vapour activity due to the swelling of the membrane by water (Metz et al., 2005; Sijbesma et al., 2008). For glassy polymers such as polyimides membranes (Chen et al., 2011; Ansaloni et al., 2014), the presence of water induces a decrease of the gas permeabilities due to competitive sorption. As water has a very high critical temperature, it competes very strongly with others penetrants for adsorption sites in the "Langmuir" voids of the polymer (Chern et al., 1983) and a decrease in solubility is observed. If the polymer is hydrophobic, water molecules interact preferentially, resulting in the formation of clusters (Chen et al., 2011; Azher et al., 2014). This can result either in an increase of the permeability due to swelling or in a decrease due to pore filling and blocking. To our knowledge, the impact of water on gas permeation in PIM-1 is addressed only in one study (Scholes et al., 2015). In addition, SOx and NOx in presence of water vapour create an acid environment that can attack the polymer and modify its properties.

This work studies the permeability of water vapour, nitrogen and carbon dioxide through PIM-1 membrane and the effect of the minor components. Gas permeation parameters (permeability and selectivity) were measured for pure and mixed gases at different humidity content on fresh PIM-1 membranes and PIM-1 membranes exposed to a flue gas mixture. The impact of the water and of flue gas on the chemical structure of PIM1 was also characterised by FTIR analysis.

2. Experimental part

2.1. Materials

PIM-1 was kindly provided in powder form by the University of Manchester, UK (Prof. Peter Budd). Nitrogen and carbon dioxide were purchased from BOC and dried before use. The synthetic flue gas mixture (10 ppm NO, 100 ppm SO_2 and 16% CO_2/N_2) was purchased from BOC and used without purification.

Infrared spectra were recorded using attenuated total reflectance (ATR) mode of the Perkin Elmer Frontier FTIR spectrometer in a spectral range of 1000-4000 cm^{-1} with a resolution of 4 cm^{-1} and an average of 10 scans.

2.2. Membrane preparation

PIM-1 membranes were casted from a filtered 2% wt. chloroform solution (VWR, UK). The membranes were dried initially at room temperature for 3 days and then in a vacuum oven at 80° C for 1 day. The films were soaked in a methanol solution for 2 hours to reverse prior film formation history (Budd et al., 2005). After removal from methanol, the films were dried in a vacuum oven at 120°C for two days with a final thickness ranging from 60 to 80 μm (Mitutoyo, Digimatic Disc Micrometer).

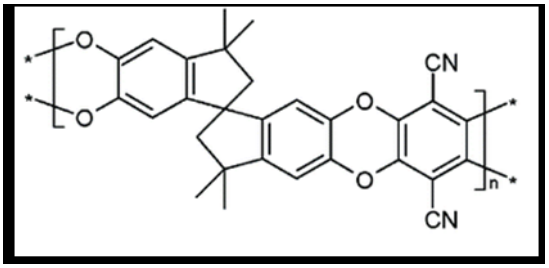

Figure 1: Chemical structure of PIM-1.

2.3. Mixed-gas permeation

The measurements of the gas permeability were made with a mixed gas - continuous flow permeation cell designed in our laboratory (Fig. 2). Pure gases (CO_2 or N_2) or a gas mixture (CO_2 + N_2) (100 Ncc/min) are fed to the system with mass flow controllers (Bronkhorst Company, Netherlands). Part of the stream is directed to a saturator filled with water and the humidity content of the feed is controlled by adjusting the relative flow rate of the dry mixture and the wet mixture with a needle valve. The total pressure of the humid feed and retentate streams are controlled by a back pressure controller (Bronkhorst Company, Netherlands) and the permeate stream is collected using a helium sweep gas with a controlled flow rate (5 Ncc/min, Bronkhorst Company, Netherlands). The permeation cell, which is immersed in a water bath in order to maintain a constant temperature (35 °C). All the tubing is heated to 100 °C with heater ropes in order to avoid any condensation in the rig.

The relative humidity and the CO_2 concentration of the feed stream are measured using respectively a humidity sensor (developed in-house based on the Honeywell HIH4000 chip) and a CO_2 sensor (Cozir Gas Sensing Solution, UK). For the permeate stream, the relative humidity is measured using a humidity sensor and the gas concentrations (CO_2 and N_2) are determined with a mass spectrometer (Proline, AMETEK). The temperature of each stream is measured using a thermocouple (K insulated 1.5 mm thermocouple). Two mixtures of nitrogen and carbon dioxide, 15 mol% and 9 mol% of CO_2 in N_2, were used for the experiments. The compositions were chosen to represent flue gas respectively from a coal-fired power plant and a gas-fired power plant.

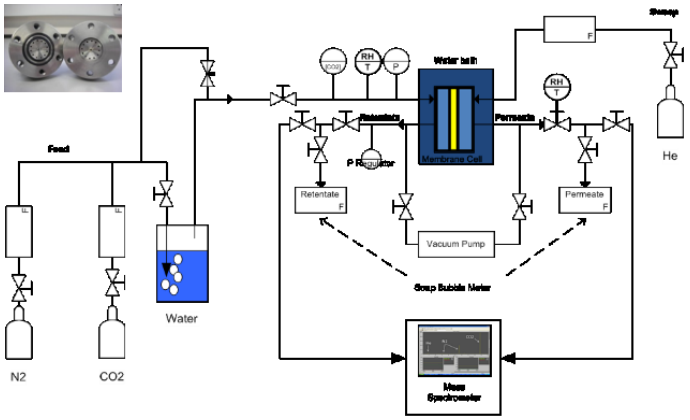

Figure 2: Water vapour permeation apparatus.

A fresh membrane was used for each experimental run that consisted in firstly the measurement of the dry mixture, and secondly the wet mixture at the chosen water vapour activity. Between two runs, the rig was evacuated until the humidity sensor detects no water, approximately 10 hours.

The temperature, the relative humidity and the gas composition of the permeate stream are recorded until the system equilibrium is reached (typically 2-3 hours). The flow rates of the retentate, permeate and feed are determined using a soap bubble flow meter.

The permeability of each gas species passing through the membrane is calculated by:

$$Perm(G) = \frac{l \,.\, Flow^P .\, X^P}{A \,.(p^F - p^P)} \quad (1)$$

Where l is the thickness of the membrane (cm), $Flow^P$ the permeate flowrate (cm^3 (STP)/s), X^P the mole fraction of the gas in the permeate stream, A the effective membrane area (cm^2), p^F and p^P the partial pressure of the gas in the feed and permeate stream respectively (cmHg).

In equilibrium conditions, the molar fraction of water is expressed by:

$$X_{H_2O} = \frac{p_w}{p_{Tot}} = \frac{RH}{100} * \frac{p_{Sat}}{p_{Tot}} \quad (2)$$

Where p_w is the water vapour partial pressure, p_{Tot} is the total pressure of the stream, p_{sat} is the saturation pressure at the stream temperature, and RH is the relative humidity measured by the humidity sensor. The ideal selectivity between two gas species i and j is calculated as the ratio of the two permeabilities.

$$\alpha_{ij} = \frac{Perm(i)}{Perm(j)} \quad (3)$$

2.4. Exposition to a flue gas mixture

A simple test was designed to study the effects of flue gas impurities on the material. A fresh membrane is exposed to dry or wet flue gas mixture in static conditions at 1 bar and room temperature. The permeability is then measured using the normal protocol, at several stages during the exposure (24, 48, 72 and 120 hours of contact).

The flue gas mixture used was composed of 10 ppm NO, 100 ppm SO_2 and 16% CO_2/N_2 (Scholes et al., 2009).

3. Results and discussion

3.1. Dry gases CO_2, N_2

The permeabilities of CO_2 and N_2 for three different CO_2 concentrations in the feed measured in dry conditions are shown in Table 1.

Table 1

CO_2/N_2 permeability for PIM-1 with dry mixtures. (PIM-1 membranes were conditioned in methanol before test. Error calculated by sample repetition)

P_{feed}=1.3 bar T= 35°C	Pure gas	15% CO_2 – 85% N_2 (coal fired power plant)	9% CO_2 – 91% N_2 (gas power plant)
PermCO_2 [Barrer]	7010 ± 420	7100 ± 426	7120 ± 427
PermN_2 [Barrer]	360 ± 32	368 ± 33	375 ± 33
Selectivity CO_2/N_2	19.5	19	19

The PIM-1 membrane exhibits a high CO_2 permeability and selectivity, which is consistent with literature (Budd et al., 2008; Budd et al., 2005). This high permeability is related to the high solubility of CO_2 in the microporous material that can be related to the presence of polar groups (Budd et al., 2008); the cyano groups in the polymer chain strengthen intermolecular interactions and encourage CO_2 sorption. The deviations of permeability with the CO_2 concentration are in the range of the experimental error, which indicates that no plasticization occurs at this low pressure as reported by other authors (Du et al., 2012; Li et al., 2014).

It is worth noting that the experiments were run on samples after the methanol treatment that swells the polymers and eliminates any trace of casting solvents. The permeability after the treatment is almost 2-fold compared to native PIM-1 (Table 2).

Table 2

CO_2/N_2 permeability for PIM-1 with dry mixtures for two different states (Error calculated by sample repetition).

P_{feed}=1.3 bar T= 35°C	PIM-1 MeOH treatment	PIM-1 Native
PermCO_2 [Barrer]	7010 ± 420	2640 ± 158
PermN_2 [Barrer]	360 ± 32	210 ± 28
Selectivity CO_2/N_2	19.5	12.5

3.2. Wet pure gases

The experimental results are reported in Figure 3, in terms of normalized gas permeability, defined as the ratio between humid gas (Perm) and dry gas (Perm^0) permeability.

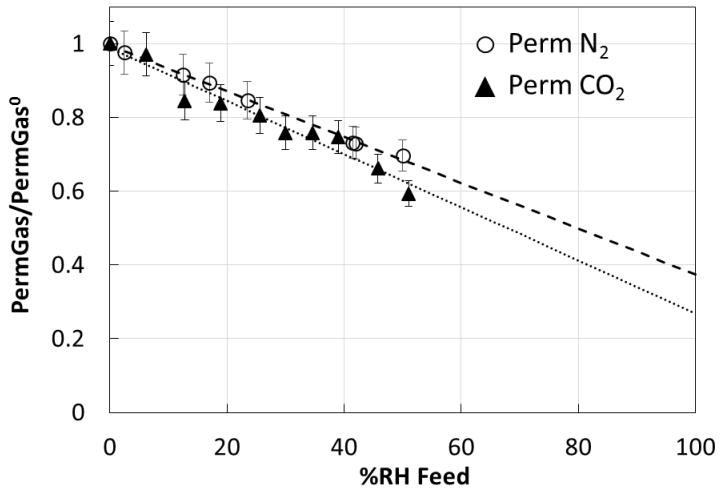

Figure 3: Normalized gas permeability, Perm/Perm^0, defined as the ratio between humid gas (Perm) and dry gas (Perm^0) permeability for PIM-1 at 35°C, for CO_2 and N_2 (The lines are for guidance only). (Error calculated by sample repetition)

The addition of moisture in the feed induces a decrease in the CO_2 permeability of PIM-1 membranes; at 11 %RH, which is the water content in a typical flue gas from coal fired power plant, the decrease is 16% compared to the dry value, at 45 %RH is 44% and finally at 60 %RH is 55%. Other authors reported similar decrease of the gas permeability (Chen et al., 2011; Ansaloni et al., 2014) for glassy polymers. This behaviour can be related to a competing sorption process for water. The polar groups, cyano and/or ether moieties of the PIM-1, strongly interact with water, and therefore they become less accessible to CO_2. Moreover, as PIM-1 is highly hydrophobic (Budd et al., 2004; Adymkanov et al., 2008, Zhang et al., 2015), water clustering can occur inside the membrane hindering the transport of CO_2 and reducing the CO_2 diffusivity.

Extrapolating the data in the limit of water saturated stream, the CO_2 permeability would decline to 73% of its original value. Budd et al. (2005) have also noticed a similar change for a PIM-1 membrane put in contact with liquid water with a decrease from 12600 Barrer (dry state) to 1550 Barrer (in contact with liquid water). Yampolskii et al. (2010) showed using FTIR spectroscopy that water associates form strong bonds with oxygen atoms of the PIM-1 polymer chain which leads to a reduction of the microporosity size and therefore of the permeability.

A decrease in nitrogen permeability is also observed with increasing relative humidity in the feed stream (Figure 3). However, at high water activity, the water has a lower influence on the nitrogen transport. At %RH approaching 100%, the N_2 permeability would decrease to 62% of its original value. N_2 permeability is affected only by the blocking effect of the clustered water molecules (Low et al., 2013). Therefore, the permeability decrease for N_2 in PIM-1 membrane under humid conditions is lower than for CO_2 leading to a decrease in selectivity.

The effect of water on gas permeability was also tested at different temperature in order to understand how process conditions can be used to favour the separation process. Figure 4 shows the change in the

CO_2 permeability coefficients of PIM-1 under humid conditions at two temperatures: at 50°C, the CO_2 permeability is decreased by 35% whereas at 35°C, it decreases by 45%. This suggests that operating the separation process at different temperature can be beneficial.

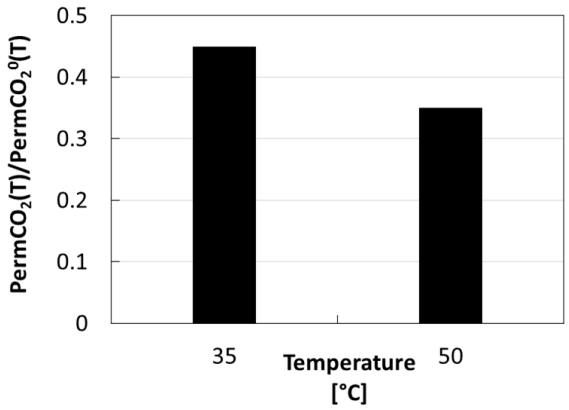

Figure 4: Normalized CO_2 gas permeability, Perm/Perm^0, defined as the ratio between humid gas (Perm) and dry gas (Perm^0) permeability for PIM-1 at 35°C and 50°C for the same water content (X_{H2O}=0.03).

3.3. Water permeability

Figure 5 summarises the vapour activity dependence of water vapour permeabilities for PIM-1 membrane under wet CO_2 and wet N_2. For both gases, there is an increase of the water permeability with the relative humidity of the feed. This is consistent with the results of others researches on glassy polymeric membranes (Chen et al., 2011; Scholes et al., 2015). This increase can be related to the increase of the water solubility at higher activity. The water vapour permeability is similar for humid CO_2 and humid N_2, within the range of the experimental error (+/- 6%) with a H_2O/CO_2 selectivity for PIM-1 around 8.4 and the H_2O/N_2 selectivity around 146.

The water vapour permeability for PIM-1 converges to a saturated gas permeability of around 58800 Barrer and 52500 Barrer for wet CO_2 and wet N_2 respectively similar to what measured by Scholes et al. (2015). Contrary to other glassy polymers (Chen et al., 2011), no plasticisation is noted with CO_2.

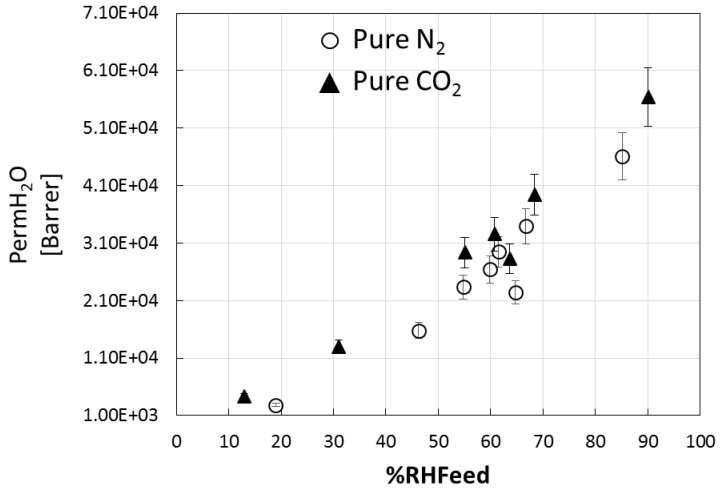

Figure 5: Water permeability in PIM-1 membranes versus the feed relative humidity for CO_2 and N_2. (Pfeed=1.3 bar, Tcell=35° C). (Error calculated by sample repetition)

3.4. FTIR analysis

The impact of the water on the PIM-1 membrane was also studied with FTIR-ATR. Figure 6 shows the ATR spectra of a PIM-1 membrane after a dry and a wet gas experiment. For the wet gas case (dashed line) the peaks related to the vibrational modes of the OH groups (1750 and 3400 cm^{-1}) are evident.

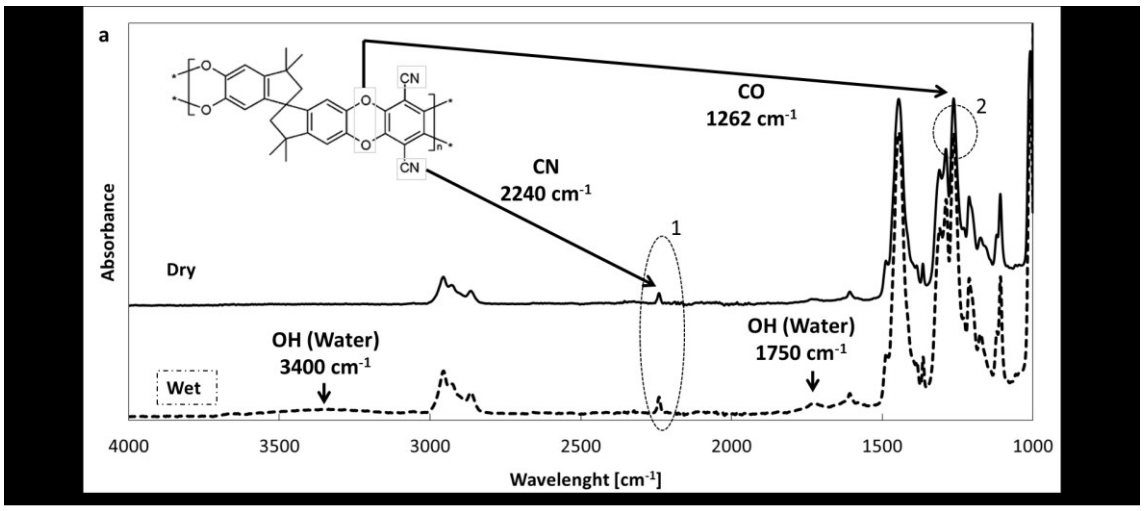

Figure 6: FTIR spectra of PIM-1 (a) in dry conditions (Plain line) and in wet conditions (Dash line).

The regions in the IR spectra around 2240 cm^{-1} and 1260 cm^{-1} are characteristic for CN and C-O-C bonds respectively and should reveal some shift in the bands positions after contact of the membrane with wet gases due to the formation of hydrogen bonds (H---N and H---O) between water and PIM-1

as reported in literature (Yampolskii et al, 2010; Chaukura, 2011). These shifts cannot be observed conclusively in the present investigation due to the limited accuracy of the FTIR system used.

3.5. Wet mixtures

Two wet mixtures were also tested in order to simulate flue gas from coal and gas fired power plants. The changes in the permeability of CO_2 and permselectivity under wet conditions are plotted respectively on the Fig. 7a and the Fig. 7b.

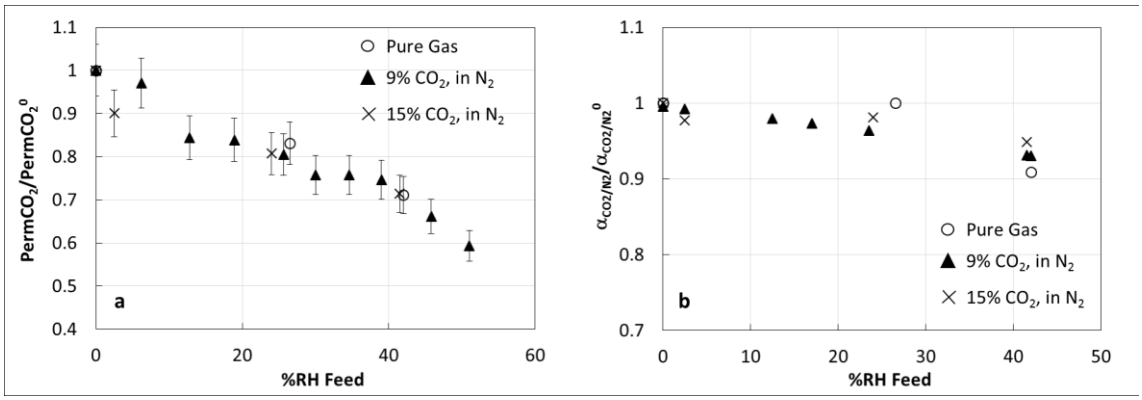

Figure 7: Variation of the CO_2 permeability in humidified CO_2-N_2 feed versus the feed relative humidity (a) and CO_2/N_2 selectivity in humidified CO_2-N_2 feed (b) of PIM1 for 3 compositions (Pure gas, 9%CO_2 in N_2, 15%CO_2 in N_2). (Pfeed=1.3 bar, Tcell=35° C. PermGas = permeability in wet conditions; PermGas^0= initial permeability in dry conditions). (Error calculated by sample repetition)

The decrease of the pure gas permeability is similar to the one of the mixture and, as in the dry condition, no CO_2 plasticization phenomena are observed.

At high water activity, the effects of the humidity content in the feed are much stronger for permeability and rather weak for permselectivity as shown in Figure 7. Scholes et al. (2015) found a similar behaviour with a decrease of the CO_2 and N_2 permeability and a constant ideal selectivity CO_2/N_2.

The presence of the water will have a negative effect on the process and needs to be considered in the process design and cost analysis.

3.6. Flue gas experiments

In order to analyse the impact of the impurities on the membrane performance, PIM-1 membranes were also exposed to a synthetic flue gas mixture, mimicking the composition of a stream coming from a coal fired power plant. First dry flue gas was used for the static contact experiment, then the test was repeated with a wet flue gas. The permeability of a mixture of CO_2 and N_2 was re-tested after each period of exposure. The normalized CO_2 and N_2 permeability results are plotted as a function of contact time in Figure 8. The interaction with dry flue gas contaminants already induces a dramatic decrease of the membrane performance, higher than the one due to simple physical aging in air. After

72 hours, the permeability of CO_2 and N_2 decrease respectively from 7010 Barrer (MeOH treated) to 3670 Barrer (Dry Flue gas exposed), and from 360 Barrer (MeOH treated) to 220 Barrer (Dry Flue gas exposed). The presence of water during the exposure affects further the performance reducing the permeability after 120 hours to 2670 Barrer for CO_2 and 165 Barrer for N_2.

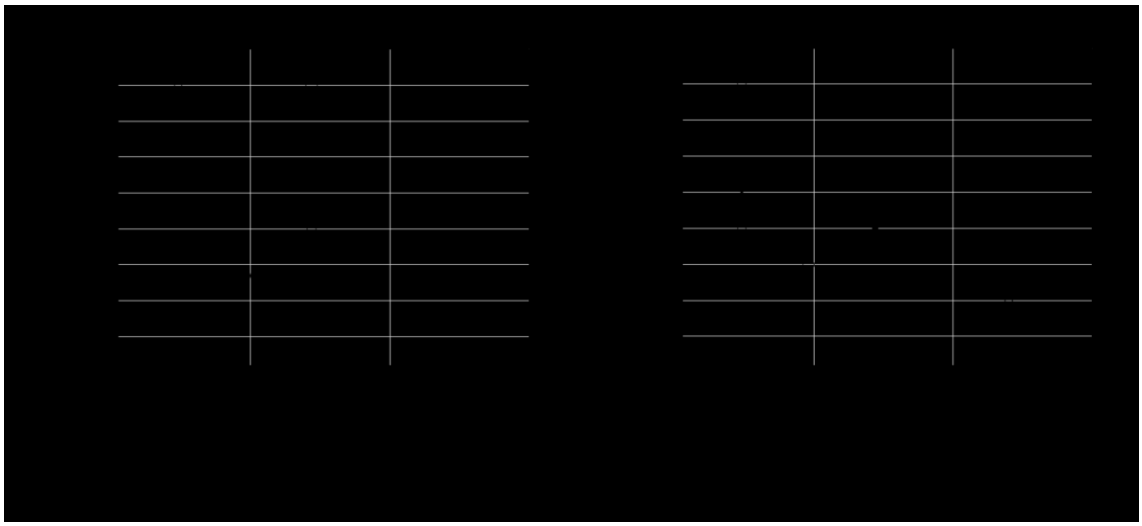

Figure 3: Variation of the CO_2 (a) and N_2 (b) permeability with the time of contact of PIM-1with flue gas. (Pfeed=1.3 bar, Tcell=35°C).

The results show that the reduction in the permeability is not only due to the relaxation of the polymer free volume but to the interactions with the impurities in the flue gas. To investigate this further, ATR-FTIR spectra of the samples exposed to flue gas were taken and compared to the MeOH treated samples. Figure 9 shows the comparison of the spectra before and after exposure to dry or wet flue gas. No notable change can be detected after exposure to dry flue gas even after permeation experiments with wet CO_2 and N_2. In the case of contact with wet flue gas, a new peak appears in the region around 1730 cm^{-1} (Figure 9) and it grows proportionally with the length of exposure.

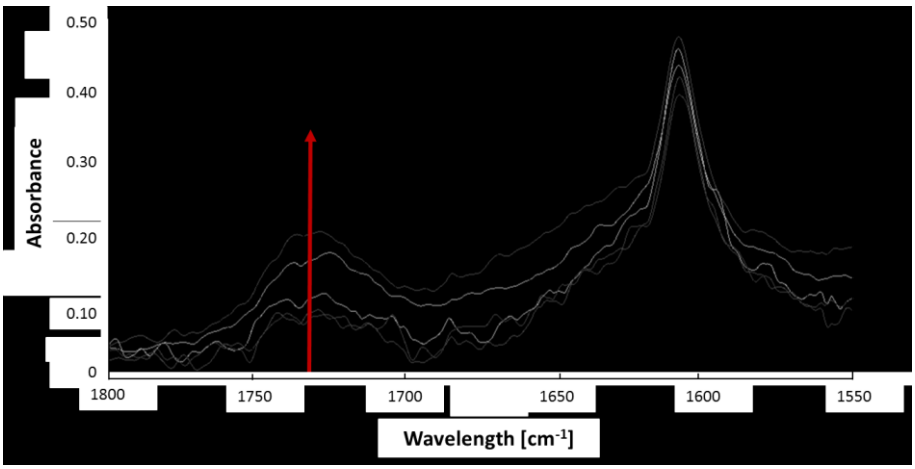

Figure 9: Increase in the band 1730 cm^{-1} with exposure time with wet flue gas.

This peak can be correlated to the stretching vibration bands of carbonyl groups (Coates, 2000) and demonstrates a permanent modification of the polymer in contact with the acid environment including water, SO_x, NO_x and CO_2. This change affects dramatically the permeability reducing it to just one third of the initial value after only 5 days of exposure and therefore needs further investigation. A possible explanation could be the acidic hydrolysis of the nitrile (CN) group on the polymer chain as supported by the simultaneous reduction of the band related to the CN group and the increase in the band related to the –OH stretching vibration around 3300 cm^{-1}. The acidic hydrolysis could be related to the reaction with H_2O and SO_2, since this is the more acidic component in the mixture.

The observed decline in permeability has to be considered in designing the separation process based on PIM materials. Process simulation calculation are usually run including minor components but not ppm level impurities (Bocciardo, et al, 2013) and this could lead to large errors in the estimation of the required membrane area. Moreover the stability of the membrane has to be taken into account in the cost estimation.

4. Conclusion

The behaviour of a PIM-1 membrane was investigated for post combustion applications, under wet conditions and after contact with flue gas. The permeability of CO_2 and N_2 declines with the humidity content of the feed, reaching a reduction of 73% and 62% respectively for a saturated stream. PIM-1 shows a high selectivity towards H_2O ($\alpha_{H2O/CO2}$=8.4 and $\alpha_{H2O/N2}$=146), with a water permeability of 58800 Barrer.

The contact with flue gas had a dramatic impact on the PIM-1 performance, with a decrease of the CO_2 permeability to 30% of the original value after only 120 hours of contact. This suggests that even mixtures permeability measurements are not sufficient to evaluate membranes for post-combustion application and that a full investigation including flue gas exposure tests is crucial to properly assess the potential of the material in carbon capture application.

References

Abanades, J.C., Arias, B., Lyngfelt, A., Mattisson, T., Wiley, D.E. , Li, H., Ho, M.T., Mangano, E., Brandani S. 2015, Emerging CO2 capture systems, International Journal of Greenhouse Gas Control, 40, pp126-166.

Adymkanov, S. V. Yampol'skii, Yu. P. Polyakov, A. M. Budd, P. M. Reynolds, K. J. McKeown, N. B. Msayib, K. J., 2008, Pervaporation of alcohols through highly permeable PIM-1 polymer films, Polymer Science Serie A, 50, pp444-450.

Allam, R.J., et al. 2003, in Carbon Dioxide Recovery and Utilization (ed M. Aresta), Kluwer, Dordrecht, pp55-118.

Ansaloni, L., Minelli, M., Giacinti Baschetti, M., Sarti, G.C. 2014, Effect of relative humidity and temperature on gas transport in Matrimid®: Experimental study and modelling, Journal of Membrane Science, 471, pp392-401.

Azher, H., Scholes, C.A., Stevens, G.W., Kentish, S.E. 2014, Water permeation and sorption properties of Nafion 115 at elevated temperatures, Journal of Membrane Science, 459, pp104-113.

Bocciardo, D., Ferrari, M.C., Brandani, S. 2013, Modelling and Multi-stage Design of Membrane Processes Applied to Carbon Capture in Coal-fired Power Plants, Energy Procedia, 37, pp932-940.

Budd, P.D., Msayib, K.J, Tattershall, C.E., Ghanem, B.S., Reynolds, K.J, McKeown, N.B., Fritsch, D. 2008, Gas separation membranes from polymers of intrinsic microporosity, Journal of Membrane Science, 325, pp851-860.

Budd, P.D., McKeown, N.B., Ghanem, B.S., Msayib, K.J., Fritsch, D., Starannikova, L., Belov, N., Sanfirova, O., Yampolskii, Y., Shantarovich, V. 2005, Gas permeation parameters and other physicochemical properties of a polymer of intrinsic microporosity: Polybenzodioxane PIM-1, Journal of Membrane Science, 251, pp263-269.

Budd, P. M. Elabas, E. S. Ghanem, B. S. Makhseed, S. McKeown, N. B. Msayib, K. J. Tattershall C. E. and Wang, D., 2004, Solution-Processed, Organophilic Membrane Derived from a Polymer of Intrinsic Microporosity, Advanced Materials, 16,pp 456-459.

Bushell, A.F, Budd, P.D., Attfield, M.P., Jones, J.T.A., Hasell, T., Cooper, A.I., Bernardo, P., Bazzarelli F., Clarizia, G., Jansen, J.C. 2013, Nanoporous Organic Polymer/Cage Composite Membranes, Angewandte Chemie, 52, pp1253-1256.

Chaukura, N. 2011, Thesis, School of Chemistry, University of Manchester.

Chen, G.Q., Scholes, C.A, Qiao, G.C, Kentish, S.E. 2011, Water vapor permeation in polyimide membranes, Journal of Membrane Science, 379, pp479-487.

Chern, R.T., Koros, W.J., Sanders, E.S., Yui, R. 1983 “Second component” effects in sorption and permeation of gases in glassy polymers, Journal of Membrane Science, 15, pp157-169.

Coates, J. 2000, Interpretation of Infrared Spectra, A Practical Approach., in Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), John Wiley & Sons Ltd, Chichester, pp. 10815–10837.

Davison, J. 2007, Performance and costs of power plants with capture and storage of CO_2, Energy, 32, pp1163-1176.

Du, N., Dal-Cin, M.M, Robertson, G.P., Guiver, M.D. 2012, Decarboxylation-Induced Cross-Linking of Polymers of Intrinsic Microporosity (PIMs) for Membrane Gas Separation, Macromolecules, 45, pp5134-5139.

Han, S.H., and Lee, Y.M. 2011, in Membrane Engineering for the Treatment of Gases Vol.1, (ed E. Drioli and G. Barbieri), Royal Society of Chemistry, pp84-124.

Ho, M.T., Allinson, G.W., and Wiley D.E. 2008, Reducing the Cost of CO2 Capture from Flue Gases Using Membrane Technology, Industrial & Engineering Chemistry Research, 47, pp1562–1568.

Krishnamurthy, S., Rao, V.R., Guntuka, S., Sharratt, P., Haghpanah, R., Rajendran, A., Amanullah, M., Karimi, I.A., Farooq, S. 2014, CO2 capture from dry flue gas by vacuum swing adsorption: a pilot plant study. AIChE Journal 60, 1830-1842.

Leimbrink , M., Kunze, A.K., Hellmann, D., Górak, A., Skiborowski, M. 2015, Conceptual Design of Post-Combustion CO2 Capture Processes - Packed Columns and Membrane Technologies, Computer Aided Chemical Engineering, 37, pp1223–1228.

Li, F.Y., Xiao, Y., Chung, T.S., Kawi, S. 2012, High-Performance Thermally Self-Cross-Linked Polymer of Intrinsic Microporosity (PIM-1) Membranes for Energy Development, Macromolecules, 45, pp1427-1437.

Li, P., Chung, T.S., Paul, D.R. 2013, Gas sorption and permeation in PIM-1, Journal of Membrane Science, 432, pp50-57.

Li, P., Chung, T.S., Paul, D.R. 2014, Temperature dependence of gas sorption and permeation in PIM-1, Journal of Membrane Science, 450, pp380-388.

Low, B.T., Zhao, L., Merkel, T.C., Weber, M., Stolten D. 2013, A parametric study of the impact of membrane materials and process operating conditions on carbon capture from humidified flue gas, Journal of Membrane Science, 431, pp139-155.

Metz, S.J., Van de Ven, W.J.C., Potreck, J., Mulder, M.H.V, Wessling, M. 2005, Transport of water vapor and inert gas mixtures through highly selective and highly permeable polymer membranes, Journal of Membrane Science, 251, pp29-41.

Robeson, L.M. 2008, The upper bound revisited, Journal of Membrane Science, 320, pp390-400.

Sijbesma, H., Nymeijer, K., Van Marwijk, R., Heijboer, R., Potreck, J., Wessling, M. 2008, Flue gas dehydration using polymer membranes, Journal of Membrane Science, 313, pp263-276.

Scholes, C.A., Jin, J., Stevens, G.W., Kentish, S.E. 2015, Competitive permeation of gas and water vapour in high free volume polymeric membranes, Journal of Polymer Science, Part. B: Polymer Physics, 53, pp719-728.

Scholes, C.A., Kentish, S.E, Stevens, G.W. 2009, Effects of minor components in carbon dioxide capture using polymeric gas separation membranes, Separation and Purification Reviews, 38, pp1-44.

Spigarelli, B. P., Kawatra, S.K. 2013, Opportunities and challenges in carbon dioxide capture, Journal of CO2 Utilization, 1, pp69–87.

Thomas, S., Pinnau, I., Du, N., Guiver, M.D. 2009, Pure- and mixed-gas permeation properties of a microporous spirobisindane-based ladder polymer (PIM-1), Journal of Membrane Science, 333, pp125-131.

Yampolskii, Y., Alentiev, A., Bondarenko, G., Kostina, Y., Heuchel, M. 2010, Intermolecular Interactions: New Way to Govern Transport Properties of Membrane Materials, Industrial & Engineering Chemistry Research, 49, pp12031-12037.

Yazdanfara, J., Mehrpooyaa, M., Yousefia, H., Palizdarb, A. 2015, Energy and exergy analysis and optimal design of the hybrid molten carbonate fuel cell power plant and carbon dioxide capturing process, Energy Conversion and Management 98, pp 15–27.

Zhang, C. Li, P. and Cao, B., 2015, Electrospun Microfibrous Membranes Based on PIM-1/POSS with High Oil Wettability for Separation of Oil–Water Mixtures and Cleanup of Oil Soluble Contaminants, Industrial & Engineering Chemistry Research, 54, pp 8772-8781.